Spin-Generalized SCF Wavefunctions for H_2O, OH, and O*

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Wavefunctions from spin-generalized SCF calculations using the GF method, are reported for H_2O, OH, and O. Three different basis sets are examined for each of these systems. The shapes and angles between the localized GF orbitals are described in some detail. It is shown that the resulting GF orbitals change in a chemically reasonable manner as we proceed from O to OH to H_2O. The dipole and quadrupole moments, electric fields, field gradients, densities, and potentials are reported for the GF wavefunctions.

I. INTRODUCTION

We have previously discussed the GF method,[1,2] a generalization of the Hartree–Fock (HF) method for electronic wavefunctions, which allows all of the spatial orbitals to be different (i.e., no double occupations), but which leads to the correct spin symmetry for the many-electron wavefunction. As discussed before,[3] the GF method leads to a wavefunction equivalent to the one which would be obtained by optimizing the orbitals of a spin-projected Slater determinant *after* the projection. Thus these orbitals are equivalent to those which would be obtained by the spin-polarized extended Hartree-Fock (SPEHF) method.[4] GF wavefunctions have been previously reported for several molecules including H_2,[3] LiH,[3] Li_2,[2] CH_3,[2] and CH_4.[2] Here we report the localized GF wavefunctions for the ground states of H_2O ($^1A_1$), OH ($^2\Pi$), and O (^3P), and compare the changes in the orbitals as we proceed from O atom to OH to H_2O. We will see that the orbitals of these systems change in a reasonable and continuous way and lead to a perspicacious description of the bonding in H_2O and OH.

II. THE WAVEFUNCTIONS

In the HF method[5] the total wavefunction is a Slater determinant

$$\mathcal{A}\Phi\chi, \tag{1}$$

where $\mathcal{A}$ is the antisymmetrizer,[6] Φ is a product of spatial orbitals

$$\Phi=\phi_{1a}(1)\phi_{2a}(2)\cdots\phi_{na}(n)\phi_{1b}(n+1)\cdots\phi_{mb}(N), \tag{2}$$

and χ is a product of one-electron spin functions

$$\chi=\alpha(1)\alpha(2)\cdots\alpha(n)\beta(n+1)\cdots\beta(N). \tag{3}$$

For the H_2O molecule we have $n=m=5$ ($N=n+m$), and in order that the wavefunction (1) be a singlet state, we force

$$\phi_{ia}=\phi_{ib}, \qquad i=1,\cdots m; \tag{4}$$

that is, we take the orbitals as doubly occupied. However, if we pull one H off to get OH+H, we need five orbitals to describe OH (four doubly occupied and one singly occupied), and one for the H. Thus the dissociated molecule requires at least six different orbitals, and since the HF wavefunction for H_2O has only five different orbitals, the HF wavefunction for H_2O cannot possibly dissociate into the HF wavefunction for OH+H. It is this improper dissociation of HF wavefunctions which has prevented detailed examinations of the nature of bonding by gradually bringing, e.g., OH and H together and following the changes which occur in the orbitals.

In order to get around this problem we replace the $\mathcal{A}$ in (1) by the group operator,[7] G_f^γ, which simultaneously takes care of both the Pauli principle and the spin symmetry. Thus we take the wavefunction as

$$G_f^\gamma\Phi\chi, \tag{5}$$

where Φ and χ are still given by Eqs. (2) and (3), but now it is not necessary to place restrictions on the orbitals of Eq. (2) as in Eqs. (4). The wavefunction in (5) has the correct spin symmetry for all choices of the orbitals ϕ_{ia} and ϕ_{ib}. The G_f^γoperator is defined in terms of Young's orthogonal units[8] O_{rf}^γ and $\omega_{\bar{r}\bar{f}}^{\bar{\gamma}}$ which operate on spatial and spin functions, respectively,[7]

$$G_f^\gamma=\sum_r \zeta_{\sigma_{rf}} O_{rf}^\gamma \omega_{\bar{r}\bar{f}}^{\bar{\gamma}}.$$

Since the many-electron Hamiltonian, $\mathcal{H}$, is independent of spin, the total energy becomes[7]

$$E=\langle\Phi\mid\mathcal{H}\mid O_{ff}\Phi\rangle/\langle\Phi\mid O_{ff}\Phi\rangle. \tag{6}$$

That is, the spin terms immediately cancel out and the energy is the same as if the many-electron wavefunction were spinless with the form

$$O_{ff}\Phi. \tag{7}$$

The O_{ff} operator can be written as[9]

$$O_{ff}=(f^\gamma/n!m!N!)N_f P_f N_f, \tag{8}$$

where f^γ is a constant and N_f and P_f are just the Young column antisymmetrizer and row symmetrizer, respectively,[8] for the f tableau. In this case, N_f antisymmetrizes coordinates 1 through n and $n+1$ through $N=n+m$, and P_f symmetrizes 1 and $n+1$, 2 and $n+2$, 3 and $n+3$, etc. Thus we can write

$$N_f=\{1,2,\cdots n\}'\{n+1,\cdots,N\}', \tag{9}$$

$$P_f=\{1,n+1\}\{2,n+2\}\cdots\{m,n+m\}, \tag{10}$$

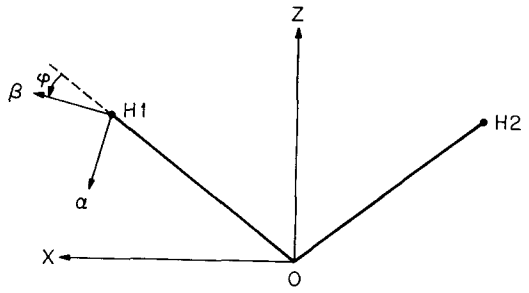

FIG. 1. Coordinates for H_2O. The Y axis is perpendicular to the plane of the molecule.

where $\{\}'$ indicates the antisymmetrizer and $\{\}$ indicates the symmetrizer. Alternative forms for (5) are[7]

$$G_f{}^\gamma\Phi\chi = f^\gamma\mathcal{A}[\Phi(\omega_{\bar{f}\bar{f}}{}^\gamma\chi)] \tag{11}$$

and

$$G_f{}^\gamma\Phi\chi = f^\gamma\mathcal{A}[(O_{ff}{}^\gamma\Phi)\chi]. \tag{12}$$

From form (11) we see that the GF wavefunction is like a Hartree–Fock wavefunction in which the spin function χ is replaced by

$$\omega_{\bar{f}\bar{f}}\chi, \tag{13}$$

which is always an eigenfunction of S^2. Here we have

$$\omega_{\bar{f}\bar{f}} = (f^\gamma/n!m!N!)P_{\bar{f}}N_{\bar{f}}P_{\bar{f}}, \tag{14}$$

where

$$P_{\bar{f}} = \{1, 2, \cdots n\}\{n+1, \cdots, N\},$$
$$N_{\bar{f}} = \{1, n+1\}'\{2, n+2\}'\cdots\{m, N\}'. \tag{15}$$

Alternatively from Eq. (12) we could view the GF wavefunction as one in which the Φ of the HF wavefunction is replaced by $O_{ff}\Phi$. Of course, using either form (11) or (12) would still result in the expression (6) for the total energy after summing over all the spins and using Eqs. (16), (17), and (4) of Ref. 7. Because of the N_f in (8), the orbitals $\{\phi_{ia}\}$ can be taken as orthogonal[1] as can the orbitals $\{\phi_{ib}\}$.

TABLE I. Coefficients and exponents for the oxygen ($9s$, $5p$, $1d$) and hydrogen ($4s$) Gaussian primitives.

Exponents[a]	Coefficients[a,b]	Type[d]	Contraction[b]
	Hydrogen		
19.2406[c]	0.03283	$1s$	
2.8992[c]	0.23121	$1s$	$1s$
0.6534[c]	0.81724	$1s$	
0.1776[c]	1.0	$1s$	$1s'$
	Oxygen		
7816.54	0.00203	$1s$	
1175.82	0.01544	$1s$	
273.188	0.07377	$1s$	$1s$
81.1696	0.24761	$1s$	
27.1836	0.61183	$1s$	
3.4136	0.24120	$1s$	
9.5322	1.0	$1s$	$1s'$
0.9398	1.0	$1s$	$2s$
0.2846	1.0	$1s$	$2s'$
35.1832	0.01958	$2p$	
7.9040	0.12419	$2p$	$2p_{x,y,z}$
2.3051	0.39473	$2p$	
0.7171	0.62738	$2p$	
0.2137	1.0	$2p$	$2p_{x,y,z}'$
0.760	1.0	$3d_{x^2}$	$3d_{x^2}$
0.760	1.0	$3d_{y^2}$	$3d_{y^2}$
0.760	1.0	$3d_{z^2}$	$3d_{z^2}$
0.760	1.0	$3d_{xz}$	$3d_{xz}$
0.760	1.0	$3d_{yz}$	$3d_{yz}$

[a] s and p exponents from S. Huzinaga, Ref. 18.
[b] s and p contractions from T. H. Dunning, Ref. 19.
[c] These exponents have been scaled to approximate a Slater orbital with an exponent of 1.2.
[d] By $3d_{x^2}$ we mean $Nx^2\exp(-\zeta r^2)$, where N is a normalization factor; i.e., $3d_{x^2}$ is *not* a pure d orbital. Thus $(3d_{x^2}+3d_{y^2}+3d_{z^2}) = Nr^2\exp(-\zeta r^2)$ is a (unnormalized) $3s$ Gaussian orbital.

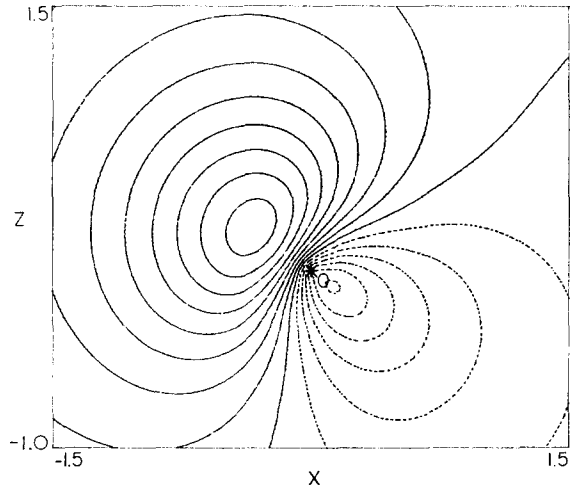

FIG. 2. One of the a LGF valence orbitals of O (plotted in the plane containing $\nabla\phi_i$). The first solid contour is the node. The other solid lines are positive contours and the dashed lines are negative contours. The interval between contours is 0.1 a.u.

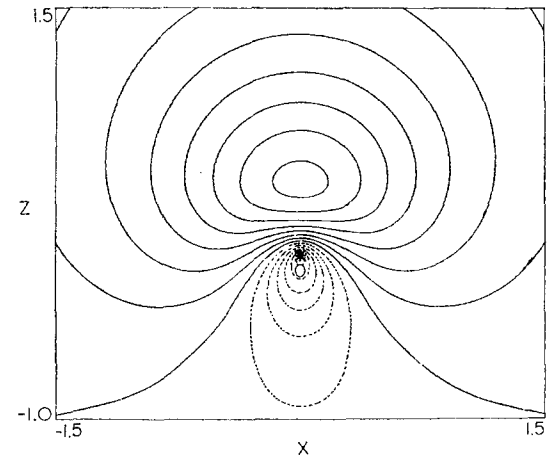

FIG. 3. One of the b LGF valence orbitals of O (plotted in the plane containing $\nabla\phi_i$). See Fig. 4 for contour values.

TABLE II. The LGF orbitals for the ground state of H_2O ($^1A_1$) using the [521/2] basis.

	a orbitals			*b* orbitals		
	Core	Nonbond[a]	Bond[a]	Core	Nonbond[a]	Bond[a]
H_1 $1s$	−0.00621	0.01120	0.11743†	−0.00919	0.03229	0.45442†
$1s'$	0.00199	0.02727	0.05282†	0.00186	0.03617	0.18589†
H_2 $1s$	−0.00621	0.01120	−0.01164†	−0.00919	0.03229	−0.03834†
$1s'$	0.00199	0.02727	−0.02725†	0.00186	0.03617	−0.05056†
O $1s$	0.59692	0.03332	−0.03076	0.59192	0.03258	−0.01784
$1s'$	0.48959	0.07615	−0.06834	0.47687	0.06797	−0.03351
$2s$	−0.10953	−0.37444	0.34759	−0.04424	−0.22865	0.10239
$2s'$	−0.05620	−0.24236	0.12277	−0.07298	−0.44557	0.07584
$2p_x$	0.0	0.0	0.56705*	0.0	0.0	0.23096*
$2p_x'$	0.0	0.0	0.11940*	0.0	0.0	0.16126*
$2p_y$	0.0	0.61435*	0.0	0.0	0.39163*	0.0
$2p_y'$	0.0	0.15583*	0.0	0.0	0.42294*	0.0
$2p_z$	0.00859	0.41436	0.41627	0.01869	0.22249	0.20010
$2p_z'$	0.00431	0.10587	0.09161	0.01761	0.22915	0.18946
$3d_{x^2}$	−0.00792	−0.02328	0.00978	0.00387	0.00543	0.01644
$3d_{y^2}$	0.00045	0.01054	−0.01148	0.00245	−0.02018	−0.00263
$3d_{z^2}$	−0.00237	0.03462	0.03681	0.00404	0.00677	0.02104
$3d_{xz}$	0.0	0.0	0.03242*	0.0	0.0	0.03629*
$3d_{yz}$	0.0	0.03757*	0.0	0.0	0.01069*	0.0

[a] Other nonbonding and bonding orbitals are obtained by changing the sign of functions denoted by * and interchanging the coefficients for H_1 and H_2 basis functions denoted by †.

In the GF method we require that the energy, Eq. (6), be stationary under variations of the orbitals in Φ. This results in the equations

$$H_a\phi_{ia}=\epsilon_{ia}\phi_{ia}, \qquad i=1, 2, \cdots, n$$

$$H_b\phi_{ib}=\epsilon_{ib}\phi_{ib}, \qquad i=1, 2, \cdots, m, \tag{16}$$

for the optimum orbitals. That is, we have two one-particle Hamiltonians to solve, rather than one as in the HF case. The construction and solution of these equations has been discussed elsewhere.[1,2]

As shown before, the spin projected wavefunction

$$\mathcal{O}^S\mathcal{A}\Phi\chi \tag{17}$$

can be written as

$$\mathcal{O}^S\mathcal{A}\Phi\chi=\mathcal{A}[\Phi(\omega\bar{f}\bar{f}\chi)] \tag{18}$$

for the case $M_S=S$. The optimum wavefunction of the form (17) where Φ and χ are product functions as in Eqs. (2) and (3), has been called the spin-polarized extended Hartree–Fock wavefunction,[3,4] which we see

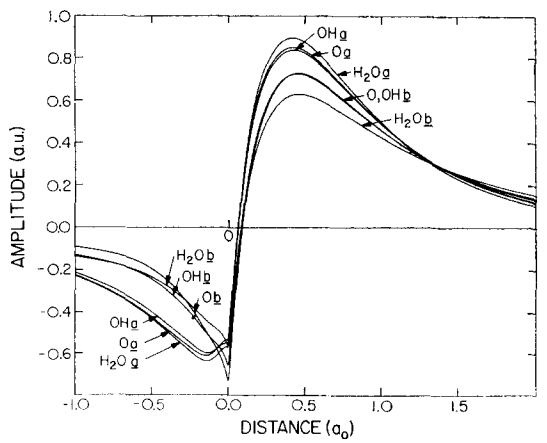

FIG. 4. The LGF orbitals of O and the LGF nonbonding orbitals of H_2O and OH (each is plotted along its axis).

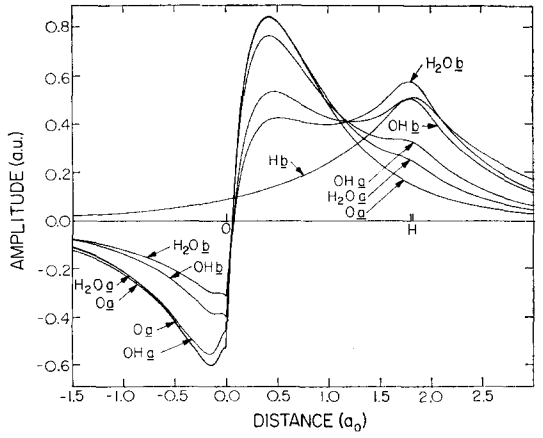

FIG. 5. The LGF bonding orbitals in H_2O and OH (each is plotted along the line connecting O and H). In addition, we show an LGF sp^3 O orbital (plotted along its axis) and the H orbital appropriate for a free hydrogen (scale 1.0).

TABLE III. The LGF orbitals for the ground state of OH ($^2\Pi$) using the [521/2] basis set.

	a orbitals				*b* orbitals		
	Core	Bond	Nonbond	Nonbond[a]	Core	Bond	Nonbond[a]
a orbitals							
H $1s$	0.00679	0.19954	0.02342	0.02342	0.00856	0.38027	0.05009
$1s'$	0.00464	0.02977	0.02696	0.02696	0.00428	0.20688	0.07374
O $1s$	0.59554	−0.02652	0.03224	0.03224	0.59472	−0.02288	0.03826
$1s'$	0.48729	−0.05715	0.07219	0.07219	0.48145	−0.04459	0.08217
$2s$	−0.09260	0.27059	−0.33365	−0.33365	−0.06542	0.18947	−0.31433
$2s'$	−0.06815	0.11796	−0.25812	−0.25812	−0.08047	0.01073	−0.45360
$2p_x$	0.0	0.0	0.0	0.56487*	0.0	0.0	0.48245*
$2p_x'$	0.0	0.0	0.0	0.22615*	0.0	0.0	0.32730*
$2p_y$	0.0	0.0	−0.65225	0.32612	0.0	0.0	0.0
$2p_y'$	0.0	0.0	−0.26113	0.13056	0.0	0.0	0.0
$2p_z$	0.00888	0.64387	0.20114	0.20114	0.01723	0.40859	0.20220
$2p_z'$	0.00309	0.20687	0.06935	0.06935	0.01078	0.19260	0.11826
$3d_{x^2}$	−0.00268	−0.00470	−0.01085	−0.01085	0.00487	−0.00439	0.01418
$3d_{y^2}$	−0.00268	−0.00470	−0.01085	−0.01085	0.00487	−0.00439	0.01418
$3d_{z^2}$	0.0	0.05455	0.01870	0.01870	−0.00001	0.06755	−0.00073
$3d_{xz}$	0.0	0.0	0.0	0.02256*	0.0	0.0	0.01763*
$3d_{yz}$	0.0	0.0	−0.02605	0.01302	0.0	0.0	0.0

* The coefficients of another nonbonding orbital are obtained from this orbital by changing the sign of the coefficients denoted *.

from Eqs. (18) and (11) is equivalent to the GF wavefunction.

III. LOCALIZATION OF ORBITALS

It is well known that for a closed-shell singlet state the many-electron Hartree–Fock determinant remains invariant under a unitary transformation among the spatial orbitals.[10] This property has been used[11,12] to find a transformation matrix which changes the Hartree–Fock symmetry orbitals to more chemically reasonable orbitals. Lennard-Jones and Pople[12] noticed that a transformation to equivalent orbitals results in an increase in the sum of the self-repulsion integrals,

$$J[\phi]=\sum_{i=1}^{N} J_{ii}, \tag{19}$$

where

$$J_{ii}=\langle\phi_i(1)\phi_i(2)\mid 1/r_{12}\mid\phi_i(1)\phi_i(2)\rangle. \tag{20}$$

Edmiston and Ruedenberg[13] have discussed several criteria which could be used to obtain the orbitals which are most localized. Of these they especially considered

TABLE IV. The LGF orbitals for the ground state of O (^{3}P) using the [521/2] basis.

	a orbitals			*b* orbitals	
	Core	Hybrid[a]	Hybrid[a]	Core	Hybrid[a]
$1s$	0.59588	−0.03099	−0.03099	0.59593	0.04257
$1s'$	0.48841	−0.06950	−0.06950	0.48299	0.09119
$2s$	−0.09823	0.33011	0.33011	−0.07183	−0.35670
$2s'$	−0.06538	0.21487	0.21487	−0.08543	−0.44300
$2p_x$	0.0	0.57582*	0.0	0.0	0.0
$2p_x'$	0.0	0.21195*	0.0	0.0	0.0
$2p_y$	0.0	0.0	0.57582*	0.0	0.0
$2p_y'$	0.0	0.0	0.21195*	0.0	0.0
$2p_z$	0.0	0.40717	−0.40717	0.0	0.50361*
$2p_z'$	0.0	0.14987	−0.14987	0.0	0.30313*
$3d_{x^2}$	−0.00235	0.00520	0.00520	0.00409	0.00872
$3d_{y^2}$	−0.00235	0.00520	0.00520	0.00409	0.00872
$3d_{z^2}$	−0.00235	0.00520	0.00520	0.00409	0.00872

[a] Another hybrid orbital is obtained by changing the signs of the coefficients marked *.

TABLE V. Angles[a] in degrees between the LGF orbitals.

Orbitals	Slater basis (21/1)		Gaussian basis [42/2]		Gaussian basis [521/2]	
	a	*b*	*a*	*b*	*a*	*b*
O	109.5	180.0	109.5	180.0	109.5	180.0
OH						
Nonbond–Bond	105.1	108.2	107.8	110.4	107.1	112.7
Nonbond–Nonbond	113.3	143.6	111.1	139.2	111.6	134.6
H_2O						
Bond–Bond	103.2	79.2	106.9	96.5	107.4	97.8
Nonbond–Nonbond	114.4	130.5	112.1	123.1	112.0	120.9
Bond–Nonbond	109.7	108.8	109.4	108.5	109.3	108.9

[a] Angles between $\nabla\phi_i$ evaluated at the *O*.

the Lennard-Jones–Pople criterion of maximizing $J[\phi]$. In addition, they proposed a simple method for finding the corresponding transformation matrix U. Ruedenberg and coworkers applied this approach to a number of systems[14] including H_2O.[15] Pitzer applied a similar method to C_2H_6.[16]

In order to localize GF wavefunctions, we note[1] that because of the Young antisymmetrizer N_f in Eq. (8), the GF wavefunction transforms as $(\det U^a)(\det U^b)$ under unitary transformations U^a on the orbitals $\{\phi_{ia}\}$ and U_b on the orbitals $\{\phi_{ib}\}$. Thus if we consider

$$\bar{\phi}_{ia} = \sum_{j=1}^{n} \phi_{ja} U_{ji}{}^{a},$$

$$\bar{\phi}_{ib} = \sum_{j=1}^{m} \phi_{jb} U_{ji}{}^{b}, \tag{21}$$

and if we take

$$\bar{\Phi} = \bar{\phi}_{1a}\bar{\phi}_{2a}\cdots\bar{\phi}_{na}\bar{\phi}_{1b}\cdots\bar{\phi}_{mb}, \tag{22}$$

we obtain

$$O_{ff}\bar{\Phi} = (\det U^a)(\det U^b) O_{ff}\Phi \tag{23}$$

and

$$G_f\bar{\Phi}\chi = (\det U^a)(\det U^b) G_f\Phi\chi. \tag{24}$$

Consequently, the energy and all other properties of the wavefunction are unchanged[1] by the transformations of Eqs. (21).

For the GF wavefunction we determine U^a and U^b by maximizing

$$J^a[\phi] = \sum_{i=1}^{n} J_{ia,ia} \tag{25}$$

and

$$J^b[\phi] = \sum_{i=1}^{m} J_{ib,ib}, \tag{26}$$

respectively. That is, we use a natural extension of the Lennard-Jones–Pople criterion for determining U_a and U_b. For open-shell restricted Hartree–Fock wavefunctions, the orbitals could also be localized by the

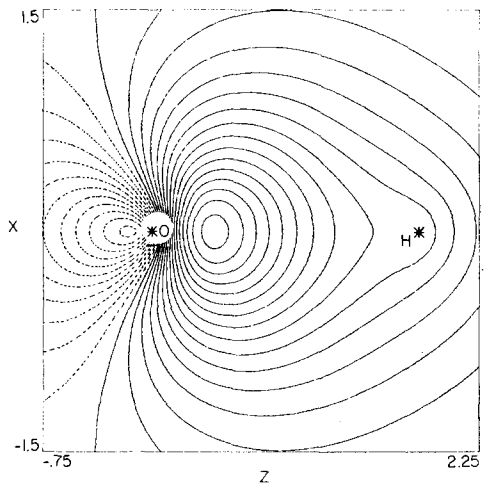

FIG. 6. The *a* LGF bonding orbital of OH. The first solid contour is the node. The other solid lines are positive contours and the dashed lines are negative contours. The interval between contours is 0.05 a.u.

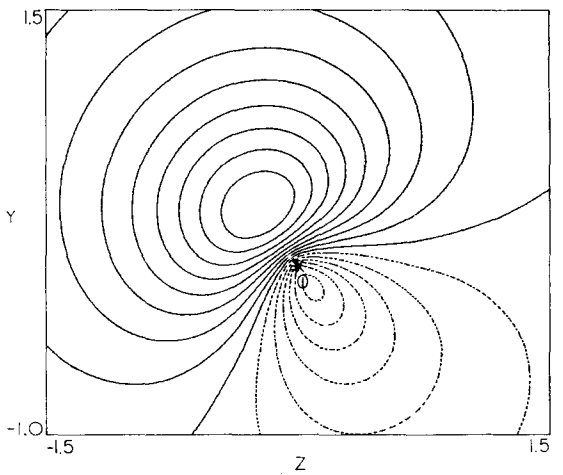

FIG. 7. One of the *a* LGF nonbonding orbitals of OH (plotted in the plane containing $\nabla\phi_i$). See Fig. 4 for contour values.

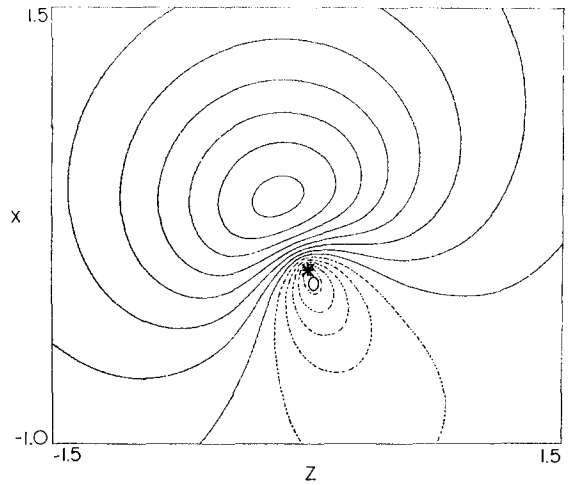

FIG. 8. One of the b LGF nonbonding orbitals of OH (plotted in the plane of these orbitals). See Fig. 4 for contour values.

above method if the doubly occupied orbitals were split and half considered as ϕ_{ia} and the other half considered as ϕ_{ib}. However, there seem to have been no such localizations reported for nonsinglet systems, such as OH and O. [*Note added in proof*: This approach has recently been applied to O_2 and NO. See D. M. Hirst and M. E. Linington, Theoret. Chim. Acta **16,** 55 (1970)].

In order to distinguish the localized GF orbitals from the canonical GF orbitals [i.e., the solutions of Eqs. (16)], we denote the former as the LGF orbitals.

IV. CALCULATIONS

The calculations were carried out for the ground states of H_2O ($^1A_1$), OH ($^2\Pi$), and O (^3P). A Slater basis set and two contracted Gaussian basis sets (centered on the nuclei) were investigated. The Slater set was a minimal basis with orbital exponents optimized for Hartree–Fock H_2O.[17] One of the Gaussian sets

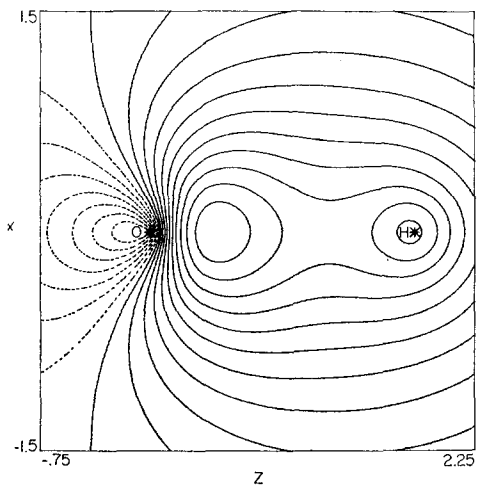

FIG. 9. The b LGF bonding orbital of OH. See Fig. 6 for contour values.

consisted of a $(9s5p/4s)$ primitive set of functions based on Huzinaga's[18] orbital exponents and contracted to a $[4s2p/2s]$ double-zeta-like basis set according to the Dunning principles.[19] This contraction increases the HF energy for H_2O by only 0.0040 a.u. (-76.0132 a.u. for (95/4) and -76.0092 a.u. for [42/2]).[19] The second Gaussian set differed from the first in having an additional set of five d-like oxygen Gaussian orbitals, d_{x^2}, d_{y^2}, d_{z^2}, d_{xz}, and d_{yz} (see Fig. 1 for the coordinates). Here by d_{x^2} we mean $Nx^2\exp(-\zeta r^2)$, where N is a normalization factor. Thus $(d_{x^2}+d_{y^2}+d_{z^2})=Nr^2\times\exp(-\zeta r^2)$ is a (unnormalized) pure $3s$ Gaussian orbital and $(2\cdot d_{z^2}-d_{x^2}-d_{y^2})$ and $(d_{x^2}-d_{y^2})$ are (unnormalized) pure $3d$ Gaussian orbitals. Since this is equivalent to adding a $3s$ orbital and a set of $3d$ orbitals to the [42/2] set, we will denote the new one as [521/2] (by symmetry we know that the d_{xy} orbital cannot be

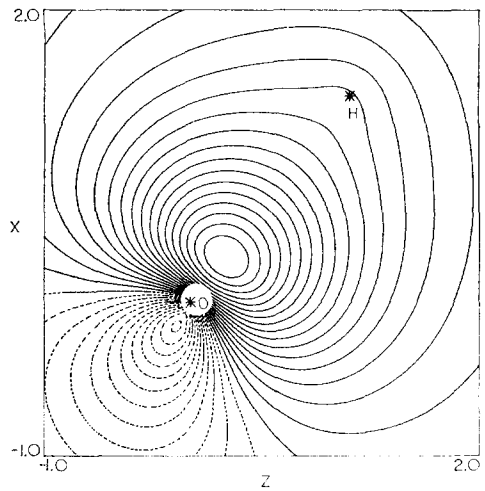

FIG. 10. One of the a LGF bonding orbitals of H_2O. See Fig. 6 for contour values.

used in the states considered here). The exponent of the d orbitals was optimized for the [521/2] H_2O Hartree–Fock wavefunction and was found to be 0.760. These basis sets were also used in the O and OH calculations in order to allow consistent comparisons between these systems.

For O and OH it was necessary to symmetry average the GF matrix Hamiltonians in order to obtain the correct spatial symmetry for the many-electron wavefunction. For these systems this is equivalent to the averaging over degenerate states used in the Roothaan open-shell formulation.[20] For OH and O this results in equivalent a type π_x and π_y orbitals and equivalent a type p_x, p_y, and p_z orbitals, respectively. As discussed below the resulting energy and properties are quite similar to those obtained when these spatial symmetry equivalence restrictions are not applied. The spatially unsymmetric wavefunctions have symmetries appropriate for the symmetry group $\mathbf{D}_{\infty h}$ rather than $\mathbf{SO}(3)$ for O and $\mathbf{C}_{2v}$ rather than $\mathbf{C}_{\infty v}$ for OH.

Irrespective of whether we apply the symmetry equivalence restriction, the final GF orbitals have been restricted to be symmetry functions of the appropriate group [**SO**(3) for O and $\mathbf{C}_{\infty v}$ for OH] by choosing the trial vectors as symmetry functions. An exception to this occurs for the [521/2] basis where d character mixed into the O s orbitals and δ character mixed into the OH σ orbitals. In these latter cases it was necessary to apply a spatial symmetry restriction in order for the GF orbitals to be symmetry functions. For the other bases it is likely that if no symmetry restrictions whatsoever are imposed, the GF orbitals of O and OH would not be exactly s and p or σ and π, respectively. (This often occurs for the UHF and GI wavefunctions of nonsinglet systems.) However the energy improvement would be expected to be small and the resulting many-electron wavefunction would not

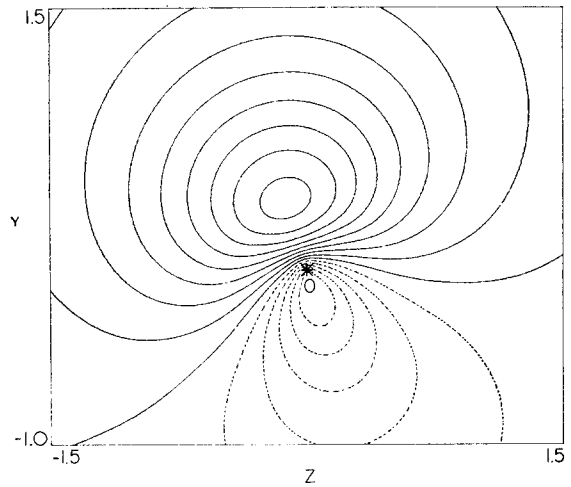

FIG. 11. One of the a nonbonding orbitals of H_2O (plotted in the plane perpendicular to the plane of the molecule). See Fig. 4 for contour values.

have the correct total symmetry (^3P for O, $^2\Pi$ for OH, and $^1A_1$ for H_2O). All the LGF orbitals reported here are those which were obtained from spatial symmetry restricted GF orbitals. In addition, for H_2O and for the OH and O wavefunctions where the symmetry equivalence restriction is applied the total wavefunction has the correct spatial symmetry.

Throughout the calculations the experimental OH and H_2O geometries have been assumed. These are 1.8342 a.u.[21] and 1.8111 a.u.[22] for the O–H distance in OH and H_2O, respectively, and 104°27 [22] for the HOH angle. The only exception to this is the Slater MBS calculation on H_2O where an O–H distance of 1.8103 a.u. was used with an HOH angle of 105°. The coordinates and geometry used for H_2O are shown in Fig. 1.

The contraction coefficients for the Gaussian bases are given in Table I. The LGF orbital coefficients in terms of these contracted coefficients for the [521/2] basis are shown in Table II for H_2O, Table III for OH, and Table IV for O.[23] In Table V we show the angles between the LGF orbitals.

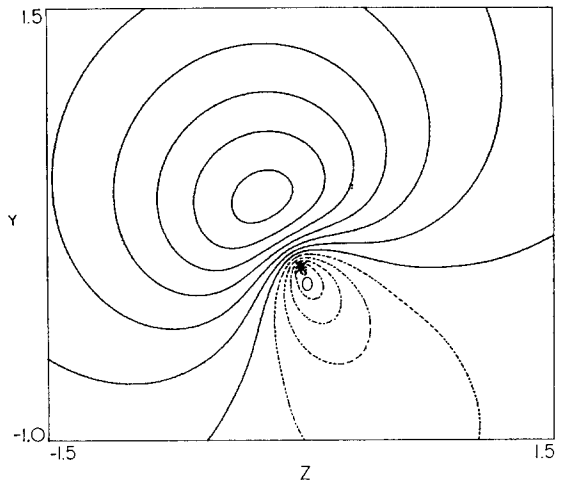

FIG. 12. One of the b nonbonding orbitals of H_2O (plotted in the plane perpendicular to the plane of the molecule). See Fig. 4 or contour values.

V. DISCUSSION OF THE LGF ORBITALS

For all three systems, H_2O, OH, and O, there are two orbitals (ϕ_{1a} and ϕ_{1b}) which are essentially the same and are referred to as oxygen 1s-like core orbitals. Since these orbitals are similar in all three systems we will omit them from the following discussion. We will also limit the discussion to the results of the [521/2] Gaussian calculation; the results for the other basis sets are quite similar.

In Fig. 2 we show a contour plot taken in the plane bisecting one of the four tetrahedrally oriented a valence orbitals of the O atom. Each of these orbitals has 75% p character[24] and can reasonably be described as an sp^3 hybrid (the symmetry restriction requires the

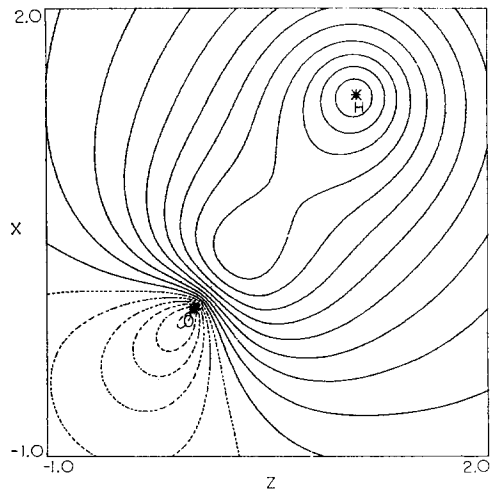

FIG. 13. One of the b LGF bonding orbitals of H_2O. See Fig. 6 for contour values.

TABLE VI. Total energies.[a]

	Basis	GF	HF	Experimental
H_2O	(10, 62/42), GTO	...	−76.05936[d]	−76.481[f]
	[521/2], GTO	−76.07804	−76.03500	
	[42/2], GTO	−76.05269	−76.0092[e]	
	(21/1), STO	−75.73384	−75.70332[f]	
OH	Cade and Huo, STO[b]	...	−75.42083	−75.780[b]
	[521/2], GTO	−75.41488	...	
	[521/2][c], GTO	−75.40992	...	
	[42/2], GTO	−75.39331	...	
	[42/2][c], GTO	−75.39321	...	
	(21/1), STO	−75.10592	−75.0600[g]	
O	(74), STO	−74.81684[j]	−74.80935[h]	−75.1101[b]
	[52], GTO	−74.81056	...	
	[52][c], GTO	−74.80548	...	
	[42], GTO	−74.80525	−74.79313[i]	
	[42][c], GTO	−74.80525	...	
	(21), STO	−74.54036	−74.54036[j]	

[a] All energies are in atomic units, 1 hartree = 27.2108 eV.
[b] P. E. Cade and W. M. Huo, Ref. 29.
[c] These wavefunctions were restricted to have the correct spatial symmetry for the many-electron wavefunction (see Sec. IV).
[d] D. Neumann and J. W. Moskowitz, Ref. 27.
[e] T. H. Dunning, Ref. 19.
[f] S. Aung, R. M. Pitzer, and S. I. Chan, Ref. 30.
[g] A. J. Freeman, Rev. Mod. Phys. **32**, 273 (1960).
[h] W. A. Goddard III, Ref. 34.
[i] Reference 27. Note that the exponents and contraction scheme for the *s* functions differs from that reported here.
[j] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).

d orbitals to add to give only a 3*s*-like contribution). For the *b* orbitals we have two orbitals separated by 180°, each containing 50% *p* character. One of these orbitals is shown in Fig. 3; they will be denoted as *sp* hybrids. Due to the higher percentage *p* character, the *a* orbitals are more directed than the *b* orbitals, i.e., on the axes of the orbitals, the *a* orbitals have higher amplitude than the *b* orbitals up to about 1.4 a_0. This can be seen from inspection of Figs. 2, 3, and 4.

From Figs. 2, 5, and 6 we see that upon formation of a bond between an oxygen tetrahedral orbital and an H atom to form OH, the sp^3 hybrid loses amplitude from the region of the O to the region around the H, and the *p* character increases slightly to 75.5%. Note that since the GF wavefunction dissociates correctly this *a* bonding orbital changes continuously to an O sp^3 hybrid as the H is pulled away. Concurrent to this transfer of amplitude the axes of the remaining *a* orbitals rearrange by about two degrees (see Table V). Thus upon formation of the OH bond the remaining three valence *a* orbitals move further apart from each other (i.e., the angle between them is greater than tetrahedral) and closer to the *a* bonding orbital. These three *a* nonbonding orbitals of OH are quite similar to the *a* tetrahedral orbitals of O (see Figs. 2, 4, and 7) except that they have lost some *p* character (down to 73.5%).

In OH we have three coplanar valence *b* orbitals. Two of the orbitals are concentrated near the O and have an angle of 134.6° between them, instead of 180° as in the O atom. These orbitals are similar in shape to the *sp* hybrids of O (see Figs. 3, 4, and 8); their *p* character has increased to 61.2%. The remaining *b* orbital has high amplitude near the H and is strongly bonding to O. Once again note that since the orbitals are not doubly occupied this orbital changes continuously to an H 1*s* orbital as the H is withdrawn from the O. From Fig. 9 we see that this orbital is much more concentrated about the bond axis than is the *a* bonding orbital.

With the addition of a second H to form H_2O we now have a singlet system containing four *a* and four *b* valence orbitals. The second H approaches one of the *a* OH nonbonding orbitals, forming a bond with 74.2% *p* character (see Fig. 10). From Figs. 4 and 5 we see that the new bonding orbital is quite similar near the O to an O atom sp^3 orbital and an OH *a* nonbonding orbital. The *a* bond–bond angle in H_2O is essentially the same as (but slightly larger than) the *a* nonbond–bond angle in OH. Thus an *a* nonbonding orbital in OH stays at nearly the same angle from the bonding orbital in OH upon the approach of the second H, forming an H_2O bond and an *a* bond–bond angle of 107.4°. The remaining two *a* nonbonding orbitals in OH move about 0.5° farther apart to 112.0° forming the two *a* nonbonding orbitals in H_2O each having 74.2% *p* character. These *a* nonbonding orbitals (see Figs. 4 and 11), which help determine the *a* bond–bond angle in H_2O have higher amplitude near the oxygen than the *a* nonbonding orbitals in OH or the sp^3 hybrid in O. However, the *b* nonbonding orbitals in H_2O (see Figs. 4 and 12) have lower amplitude near the oxygen than the *b* nonbonding orbitals in OH or the *sp* hybrids in O. The two nonbonding *b* orbitals in OH which were in the same plane with the bonding orbital now move closer together and into a plane perpendicular

TABLE VII. Orbital energies and properties of H_2O.[a,b]

	GF [521/2]	GF [42/2]	HF [521/2]	HF [42/2][d]	N–M[e]	APC[f]	Experimental
$-\epsilon(1a_{1,a})$	20.69980	20.70711	20.55383	20.5594	20.55805	20.5654	
$-\epsilon(1a_{1,b})$	20.59129	20.59469					
$-\epsilon(2a_{1,a})$	1.57821	1.59020	1.34661	1.3613	1.35224	1.3392	
$-\epsilon(2a_{1,b})$	1.35907	1.37564					
$-\epsilon(1b_{2,a})$	0.90034	0.89903	0.71326	0.7165	0.71897	0.7283	
$-\epsilon(1b_{2,b})$	0.79428	0.80124					
$-\epsilon(3a_{1,a})$	0.77487	0.77162	0.57732	0.5668	0.58222	0.5950	
$-\epsilon(3a_{1,b})$	0.61803	0.60008					0.533±0.011[l]
$-\epsilon(1b_{1,a})$	0.70928	0.71760	0.50266	0.5063	0.50685	0.5211	
$-\epsilon(1b_{1,b})$	0.51758	0.51614					0.463±0.004[l]
T	76.10192	76.12058	76.03101	···	76.00938	75.662145	
$\langle\Sigma\, 1/r_{ij}\rangle$	37.70780	37.64824	37.83124	···	37.84784	···	
μ	0.87044	1.0331	0.89092	1.0558	0.785	0.8006	0.728[g]
Θ_{xx} (c.m.)[k]	1.83246	1.82715	1.84785	1.8302	1.882	1.96241	···
Θ_{yy} (c.m.)	−1.78654	−1.69641	−1.79664	−1.7077	−1.801	−1.92490	···
Θ_{zz} (c.m.)	−0.04592	−0.13074	−0.05121	−0.1225	−0.0805	−0.03751	···
E_z (O)	−0.12039	−0.24850	−0.11683	−0.2479	−0.010	−0.070247	0.0
E_x (H)	0.04872	0.10770	0.03892	0.1000	0.0	0.001650	0.0
E_z (H)	0.02934	0.04346	0.02150	0.0366	−0.002	−0.003488	0.0
q_{yy} (H)	0.29367	0.31335	0.29073	0.3114	0.294	0.310488	0.2660±0.0005[h]
$q_{\alpha\alpha}$ (H)	0.22630	0.24742	0.22457	0.2467	0.225	0.241506	0.2026±0.0002[h]
$q_{\beta\beta}$ (H)	−0.51997	−0.56077	−0.51531	−0.5581	−0.519	−0.551994	−0.4686±0.0002[h]
φ	0.48472°	2.81122°	0.38660°	2.71667°	0.97°	0.95°	−1.26667° [h]
q_{yy} (O)	1.83137	1.93042	1.94060	2.0517	1.852	1.834756	1.73±0.01[h]
q_{xx} (O)	−1.59238	−1.68230	−1.69955	−1.8084	−1.679	−1.680384	−1.513±0.005[h]
q_{zz} (O)	−0.23899	−0.24812	−0.24104	−0.2432	−0.173	−0.154372	−0.22±0.02[h]
$\delta(r-\mathrm{O})$	294.908	295.027	294.915	295.051	299.497	···	···
$\delta(r-\mathrm{H})$	0.40012	0.42446	0.38937	0.4147	0.392	···	···
$\langle 1/r_{\mathrm{H}}\rangle$[c]	5.76161	5.74368	5.75657	5.7384	5.795	5.744	5.744[i]
$\langle 1/r_{\mathrm{O}}\rangle$[c]	23.44354	23.43973	23.44599	23.4426	23.445	23.38	···
$\langle x^2\rangle_{\mathrm{c.m.}}$[c,k]	7.23003	7.27137	7.18537	7.2315	···	···	···
$\langle y^2\rangle_{\mathrm{c.m.}}$[c]	5.54414	5.52185	5.51648	5.4916	···	···	···
$\langle z^2\rangle_{\mathrm{c.m.}}$[c]	6.44855	6.54289	6.41768	6.5128	···	···	···
$\langle r^2\rangle_{\mathrm{c.m.}}$[c]	19.22272	19.33611	19.11954	19.2359	19.181	19.51	18.2±1.1[j]

[a] All energies and properties are in atomic units.

[b] The expressions for the operators for the properties given here can be found in Ref. 27. We denote the properties as follows: ϵ=orbital energy, μ=dipole moment, Θ_{ik}=elements of quadrupole tensor, E_i(A)=components of electric field at A, q_{ii}(A)=components of electric field gradient tensor at nucleus A, $\delta(r-\mathrm{A})$=density at nucleus A, $\langle 1/r_{\mathrm{A}}\rangle$=electronic potential at A, T=total kinetic energy, $\langle\Sigma\, 1/r_{ij}\rangle$=total electron repulsion energy, and $\langle x^2\rangle$=expectation value of $\Sigma_i x_i^2$.

[c] Only the electronic contributions are given here.

[d] T. H. Dunning, Ref. 19.

[e] [10,62/42]HF calculation of Ref. 27. The geometry used here was slightly different from ours.

[f] Taken from wavefunctions IV of Ref. 30 and S. Aung, Ph.D. thesis, California Institute of Technology, 1969.

[g] W. H. Kirchoff and D. R. Lide, Jr., Ref. 31; 1 a.u.=2.541539 D.

[h] Calculated from quadrupole coupling constants reported in Ref. 33, assuming an ^{17}O quadrupole moment of −0.025*b* (see Ref. 34) and a *D* quadrupole moment of 0.002796*b* (see Ref. 36). φ is from Ref. 33.

[i] See Ref. 30.

[j] D. Eisenberg, J. M. Pochaw, and W. H. Flygare, J. Chem. Phys. **43**, 4531 (1965).

[k] c.m. denotes that this quantity was calculated with the center of mass of H_2O as the origin.

[l] W. C. Price and T. M. Sugden, Trans. Faraday Soc. **44**, 108 (1948).

to the plane of the bonding orbitals upon approach of the second proton, forming the two *b* nonbonding orbitals in H_2O having a *p* character of 68.7%. These *b* nonbonding orbitals are about 9° further apart from each other than the *a* nonbonding orbitals.

Since the *b* bonding orbitals have their highest amplitude near the H, one should not place too much importance on the *b* bond–bond angles given in Table VII for H_2O since these angles were measured at the O. But the angle is indicative of the bending of the *b* bonding orbital, which can be seen in Fig. 13. One can see from Figs. 10 and 13 and from the indicated bond–bond angles from Table VII that none of the bonding orbitals of H_2O are symmetric about an OH axis.

These results for H_2O should be compared to those of Edmiston and Ruedenberg[15] who obtained 89.8° for the bond–bond angle, and 124° between nonbonding orbitals from localizing a restricted HF wavefunction composed of a minimum basis set of Slater orbitals.

It is often suggested that the bonds in H_2O are *p* bonds. Since such bonds should be at 90°, it is suggested[25] that repulsion between positive hydrogens leads to the actual bond angle of 104.5°. Our calcula-

TABLE VIII. GF orbital energies and properties of OH.[a]

	[521/2] Unsym[h]	[521/2] Sym[h]	[42/2] Unsym[h]	[42/2] Sym[h]	HF	Experimental
$-\epsilon(1\sigma_a)$	20.67152	20.67036	20.67731	20.67607	20.61811[d]	
$-\epsilon(1\sigma_b)$	20.58758	20.58550	20.58832	20.58825		
$-\epsilon(2\sigma_a)$	1.49912	1.49914	1.51150	1.51001	1.30684[d]	
$-\epsilon(2\sigma_b)$	1.21604	1.20965	1.21976	1.22005		
$-\epsilon(3\sigma_a)$	0.73871	0.73802	0.74406	0.74324	0.66041[d]	
$-\epsilon(3\sigma_b)$	0.63072	0.62820	0.61324	0.61301		
$-\epsilon(1\pi_{x,a})$	0.61390	0.80155	0.62694	0.80051	0.57215[d]	
$-\epsilon(1\pi_{x,b})$	0.49493	0.48279	0.48549	0.48797		0.4910[f]
$-\epsilon(2\pi_{y,a})$	0.67143	0.80155	0.66263	0.80051	0.57215[d]	
T	75.43989	75.43681	75.45063	75.45080		
$\langle\Sigma\, 1/r_{ij}\rangle$	32.87772	32.88330	32.84718	32.84891		
μ	0.73684	0.73775	0.83655	0.83604	0.7005[e]	0.6531[g]
Θ_{xx} (c.m.)[c]	−1.34877	−1.35575	−1.28123	−1.29283		
Θ_{yy} (c.m.)	0.12566	0.13486	0.17479	0.18750		
Θ_{zz} (c.m.)	1.22312	1.22090	1.10644	1.10533		
E_z (O)	−0.10160	−0.10198	−0.20117	−0.20113		
E_z (H)	0.05058	0.05071	0.12180	0.12182		
q_{yy} (H)	0.19305	0.19363	0.22384	0.22357		
q_{xx} (H)	0.28005	0.27941	0.30294	0.30321		
q_{zz} (H)	−0.47310	−0.47304	−0.52678	−0.52679		
q_{yy} (O)	−2.11798	−2.05698	−2.06161	−2.00819		
q_{xx} (O)	2.63851	2.56571	2.70608	2.65473		
q_{zz} (O)	−0.52054	−0.50873	−0.64447	−0.64655		
$\delta(r-\mathrm{O})$	295.786	295.797	295.893	295.884		
$\delta(r-\mathrm{H})$	0.39328	0.39333	0.42569	0.42574		
$\langle 1/r_{\mathrm{H}}\rangle$[b]	5.32241	5.32228	5.30582	5.30598		
$\langle 1/r_{\mathrm{O}}\rangle$[b]	22.84647	22.84617	22.84347	22.84356		
$\langle x^2\rangle_{\mathrm{c.m.}}$[b,c]	4.92234	4.92930	4.90125	4.90830		
$\langle y^2\rangle_{\mathrm{c.m.}}$[b]	3.93939	3.93556	3.93058	3.92141		
$\langle z^2\rangle_{\mathrm{c.m.}}$[b]	3.20775	3.21153	3.30947	3.30953		
$\langle r^2\rangle_{\mathrm{c.m.}}$[b]	12.06948	12.07639	12.14130	12.13924		

[a] All energies and properties are in atomic units.

[b] These include only the electric contribution.

[c] c.m. denotes that this property was calculated with the center of mass of OH as origin.

[d] P. E. Cade and W. M. Huo, Ref. 29.

[e] P. E. Cade and W. M. Huo, J. Chem. Phys. **45**, 1063 (1966).

[f] P. G. Wilkinson, Astrophys. J. **138**, 778 (1963).

[g] F. X. Powell and D. R. Lide, Jr., Ref. 32.

[h] Sym implies that equivalence restrictions were imposed on the π_x and π_y orbitals and the d_{x^2}, d_{y^2}, and d_{z^2} basis functions (see Sec. IV). Unsym implies that these symmetry restrictions were not imposed.

tions do not support either of these suggestions. We saw that the a bonding orbitals have about 75% p character and can reasonably be considered as sp^3 orbitals. Thus the assumption of p bonds is not justified. In addition, we saw that the angle between the bonding and nonbonding orbitals of OH did not change appreciably when the H was bonded to the nonbonding orbital. If H repulsions were important, we would have expected this angle to increase. Although the GF orbitals lead to a reasonable explanation of the bonding in H_2O, a significant test will be whether it also does so for molecules such as H_2S, where the bonding angle is much different (92°).

In recent years Linnett[26] has proposed a novel model of bonding in which the familiar Lewis octet is replaced by a double quartet, one quartet for each spin. In Linnett's model a quartet of electrons of the same spin should be at the vertices of a tetrahedron in order to minimize the electron repulsion energy. The electrons of the molecule are then shared in such a way as to complete tetrahedral quartets about each atom often leading to a Lewis octet. Although this model is based on nonquantitative semiclassical reasoning, it does lead to compelling descriptions of some molecules, especially nonsinglet states such as O_2. It is interesting to note here that for H_2O and a number of other systems which we have considered (e.g., C_2H_2, NH, HF), the LGF orbitals are distributed in space in a way qualitatively similar to Linnett's quartets. Of course the LGF orbitals are not centered on just one atom and the bonding orbitals are paired with one orbital more near one center than the other. Water is not the best system for discussing this since there is only one octet (however note that for O, OH, and H_2O the a quartet is always within 3° of tetrahedral); C_2H_2 and BF are more appropriate and especially for C_2H_2 the results are consistent with Linnett's model. This will be discussed in more detail in a future paper,

TABLE IX. GF orbital energies and properties of O.[a]

	[521] Unsym[b]	[521] Sym[b]	[42] Unsym[b]	[42] Sym[b]	(74) STO[d]	Experimental
$-\epsilon(1s_a)$	20.73566	20.73570	20.73683	20.73677	20.73879	•••
$-\epsilon(1s_b)$	20.62570	20.62490	20.62368	20.62368	20.62834	•••
$-\epsilon(2s_a)$	1.53034	1.53072	1.52990	1.52983	1.53886	•••
$-\epsilon(2s_b)$	1.06748	1.06192	1.06237	1.06239	1.06471	•••
$-\epsilon(2p_{x,a})$	0.64725	0.84521	0.65838	0.84456	0.66813	•••
$-\epsilon(2p_{x,b})$	0.51003	0.49748	0.49743	0.49759	0.49695	0.50032[e]
$-\epsilon(2p_{y,a})$	0.71096	0.84521	0.70597	0.84456	0.71279	•••
$-\epsilon(2p_{z,a})$	0.71096	0.84521	0.70597	0.84456	0.71279	•••
T	74.81115	74.80732	74.79849	74.79850	74.81776	
$\langle\Sigma\, 1/r_{ij}\rangle$	28.44441	28.45090	28.45233	28.45242	28.42636	
Θ_{xx}	−0.94745	−0.93257	−0.93019	−0.93155	•••	
Θ_{yy}	0.47372	0.46628	0.46510	0.46578	•••	
Θ_{zz}	0.47372	0.46628	0.46510	0.46578	•••	
q_{yy}(O)	−1.66604	−1.65357	−1.65846	−1.65550	−1.71153	−1.777[c]
q_{xx}(O)	3.33208	3.30713	3.31692	3.31101	3.42306	3.554[c]
q_{zz}(O)	−1.66604	−1.65357	−1.65846	−1.65550	−1.71153	−1.777[c]
$\delta(r-\mathrm{O})$	296.516	296.530	296.519	296.518	311.5249	•••
$\langle 1/r_O\rangle$	22.25828	22.25797	22.25710	22.25711	22.25762	•••
$\langle x^2\rangle$	4.31752	4.30971	4.30665	4.30751	•••	
$\langle y^2\rangle$	3.37008	3.37714	3.37646	3.37596	•••	
$\langle z^2\rangle$	3.37008	3.37714	3.37646	3.37596	•••	
$\langle r^2\rangle$	11.05768	11.06399	11.05957	11.05943	11.24470	

[a] All energies and properties are in atomic units.

[b] Sym implies that equivalence restrictions were imposed on the p orbitals of O and the d_{x^2}, d_{y^2}, and d_{z^2} basis functions (see Sec. IV). Unsym implies that such restrictions were not imposed.

[c] Using $Q = -0.025b$ and $qQ = 0.04442$ from Ref. 34.

[d] W. A. Goddard III, Ref. 34.

[e] C. E. Moore, Natl. Bur. Std. Circ. **467**, Vol. 1 (1949).

but we note here that the LGF orbitals may provide the theoretical foundation for Linnett's model and in any case should lead to a quantitative description of bonding in terms of interpretable orbitals.

VI. DISCUSSION OF THE ENERGIES AND PROPERTIES

The GF total energies for H_2O, OH, and O are given in Table VI and compared with the HF results. We see that the [521/2] GF H_2O energy is 0.019 hartree 0.5 eV) lower than that obtained by Neumann and Moskowitz[27] (hereafter NM), the best previously reported value. Note that NM used a larger uncontracted (10, 62/42) basis. Comparing the GF and HF results for the [521/2] and [42/2] bases, we see that the GF energy is lower by 0.043 hartree in both cases, indicating that for the (10, 62/42) basis the GF energy would be about −76.102 hartree.

The bond dissociation energy of H_2O, D_e(H–OH),[28] is calculated from the [521/2] GF wavefunctions to be 0.1632 a.u. or 81% of the experimental value, 0.201 a.u.[29,30] The [521/2] total binding energy of H_2O is calculated to be 0.2675 a.u. which is 72% of the experimental value, 0.371 a.u.[29,30]

In Tables VII, VIII, and IX we show the orbital energies and several properties for H_2O, OH, and O, respectively. We see that using Koopmans' theorem,[2] the calculated first ionization potential is too large by about 12% for H_2O, 1% for OH, and 2% for O (using the [521/2] basis).

Neumann and Moskowitz[27] have already pointed out the importance of d basis functions on the O, and p basis functions on the H, for describing the dipole moment μ. Comparing the HF results we see that the inclusion of one set of O d functions accounts for about 61% of the difference between the [42/2] and NM H_2O dipole moments. The GF dipole moment was 0.02 a.u. lower than the corresponding HF value for both Gaussian sets and hence would probably be about 0.765 a.u. for the (10, 6, 2/42) basis. This compares to an experimental value of 0.728 a.u.[31] The calculated OH dipole moment also decreases significantly upon adding d basis functions but is still larger than the experimental value of 0.653 a.u.[32] For both H_2O and OH the inclusion of d basis functions significantly decreases $\langle z^2\rangle_{\mathrm{c.m.}}$.

Comparing the symmetry restricted and unrestricted GF calculations on OH, we see that the symmetry restrictions significantly decrease $\epsilon_{1\pi x,a}$ and $\epsilon_{1\pi y,a}$ but lead to small changes in the other properties in Table VIII (largest change is 7% in θ_{yy} and 3% in q_{yy}(O) and q_{xx}(O) for the [521/2] basis). This indicates that the charge distribution is not appreciably altered by the symmetry restrictions.

As has been observed before[30] the potentials at the O

and H are rather insensitive to changes in the basis. These potentials are related to the diamagnetic shielding by $\sigma_A{}^d = (e^2/3mc^2)\langle\sum 1/r_A\rangle$.

For H_2O the experimental values of the elements of the electric field gradient tensor, q_{ii}, were computed from the experimental quadrupole coupling constants of Verhoeven *et al.*[33] using the O^{17} quadrupole moment of $-0.025b$ from Goddard[34] (Schaefer *et al.*[35] obtained $-0.0256b$) and the D quadrupole moment of $+0.002796b$ from Narumi and Watanabe.[36] Here x, y, and z are the principal axes of the electric field gradient tensor at the O, α, β, and y are the principal axes at the H, and φ is the orientation angle (see Fig. 1). The resulting $q_{ii}(O)$ from the GF wavefunctions for H_2O are all closer to experiment than those from the HF wavefunctions of Neumann and Moskowitz[27] and Aung *et al.*[30] The GF values of $q_{ii}(H)$ in H_2O are quite similar to the HF values from Neumann and Moskowitz, and are more sensitive to the addition of O d functions than are the $q_{ii}(O)$.

VII. SUMMARY

We find that the LGF orbitals lead to a lucid description of the changes in bonding as we proceed from O to OH to H_2O. It appears that this same approach will generally lead to equally useful results in other systems. In particular, these calculations indicate that the LGF orbitals may provide a theoretical foundation for Linnett's double-quartet model of bonding.

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